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Orbital Interactions. 6. The Birch Reduction as a Tool for Exploring Orbital Interactions through Bonds. Through-Three-Bond Interactions¹

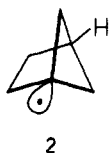
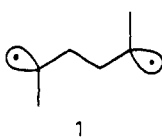
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Abstract: Product and relative rate data have been obtained for the Birch reduction (Li/liquid NH₃/tert-butyl alcohol) of a number of 1,4-methanobiphenylenes. The rates of reduction of the double bond in *exo*- and *endo*-1,4,4a,8b-tetrahydro-1,4-methanobiphenylene (*exo*- and *endo*-16) are respectively 141 and 78 times greater than the rate of reduction of norbornene. However, the reduction of the aromatic rings in *exo*- and *endo*-16 showed little enhancement compared with the rates of reduction of *exo*- and *endo*-1,2,3,4,4a,8b-hexahydro-1,4-methanobiphenylenes (*exo*- and *endo*-19), respectively. The double bonds of *exo*- and *endo*-1,4,4a,5,8,8b-hexahydro-1,4-methanobiphenylenes (*exo*- and *endo*-18) are little affected compared with norbornene. Interactions between the vacant MOs in these and other molecules were explored with the aid of extended Hückel calculations. The results of these calculations demonstrated the presence of sizable through-bond interactions in *exo*-16. However, net through-space interactions in the vacant MO manifold are predicted to prevail in *endo*-16. A causal connection between the presence of orbital interactions and the rates of Birch reduction of *exo* and *endo* compounds 16, 18, and 19 was established within the framework of the mechanism of the reaction. A linear relationship between ln (rate of reduction) of a substrate and its LUMO energy was observed.

Introduction

Hoffmann and his co-workers have delineated two distinct mechanisms which give rise to long-range interactions between remote orbitals: orbital interactions through space (OITS) and orbital interactions through bonds (OITB).²⁻⁴ The more familiar OITS result from the direct spatial overlap of the interacting orbitals.³ Consequently the magnitude of this type of interaction is strongly attenuated with distance, being negligible for interorbital separations >2.7 Å.^{2a} However, OITB are a longer range phenomenon since they are relayed by the connecting σ framework with which the interacting orbitals overlap.^{3,4} For example, extended Hückel (EH) calculations on some model dehydropolyenyl systems, C_nH_n, such as **1** ($n = 4$), show a regular exponential diminution of the

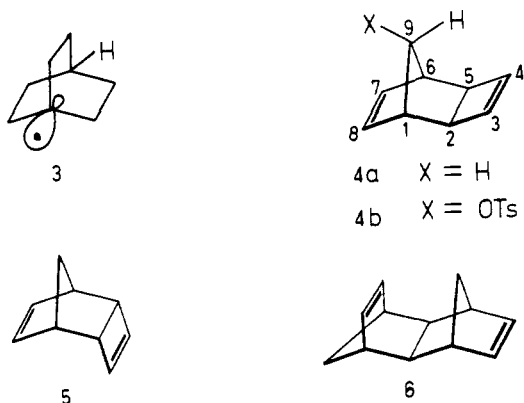


coupling of the radical lobes with distance. Nevertheless a

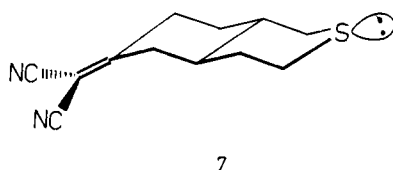
sizable interaction of 0.2 eV was calculated for a through-seven-bond interaction in C₈H₈ in which the interorbital separation is about 8.7 Å.

OITS and OITB may lead to different level orderings of the resulting MOs. Thus through-space interactions between two orbitals generally lead to the level ordering "S" below "A".^{3,5} The resulting level ordering from OITB often (but not always) depends on the parity of the number m of the intervening σ bonds, generally being "S" below "A" for even values of m and "A" below "S" for odd values of m .^{2a} Therefore, for even m , OITS and OITB reinforce one another to give a sizable net interaction. For odd m , however, the two modes of interaction oppose each other, the net outcome depending on the molecular geometry.⁶

Physical consequences of OITB have been extensively studied using spectroscopic techniques.⁸⁻¹⁰ For instance, ESR studies indicate the presence of two¹¹ through-two-bond and one through-three-bond interactions between the radical lobe and β hydrogen in **2**,¹² and triple through-three-bond interactions in **3**.¹³ Photoelectron spectroscopy (PES) has revealed through-three-bond interactions between the π orbitals in the dienes **4a**¹⁴ and **5**,¹⁵ although the net result in the latter com-

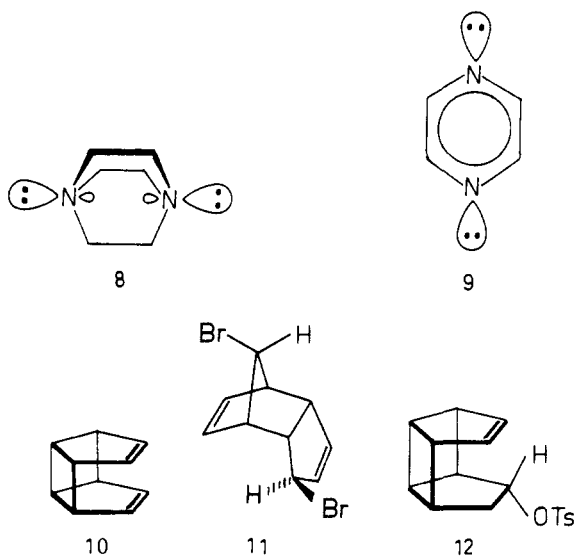


pound is small because of competing OITS. Only two reports concerning orbital interactions extending over more than three bonds have appeared. Thus Martin and Schwesinger rationalized the PES data for **6** in terms of two weak through-four-bond interactions between the π orbitals.¹⁶ Verhoeven and his co-workers¹⁷ have attributed the presence of a charge-transfer band in the UV spectrum of **7** to the operation of two



through-five-bond interactions between the nonbonding orbital of the sulfur atom and the π^* MO of the double bond.

There is a comparative dearth of documented examples of the chemical consequences of OITB,⁸ perhaps the best known being the stereospecific [$\pi 2_s + \omega 2_s + \omega 1_s$] cycloaddition reactions of 1,8-dehydronaphthalene with olefins¹⁸ and the Grob-type fragmentation reactions of 4-substituted quinuclidines.¹⁹ Disturbingly, some molecules whose physical properties are markedly changed by OITB show no evidence of these interactions in their chemical reactions. Thus the nitrogen lone pairs of Dabco (**8**) and pyrazine (**9**) exhibit normal chemical behavior²⁰⁻²² despite the presence of large through-bond interactions in these compounds.^{23,24} Although OITB have been invoked to account for the facile rearrangement of hypostrophene (**10**) to **11** with bromine,^{25,26} and for

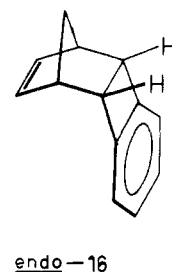
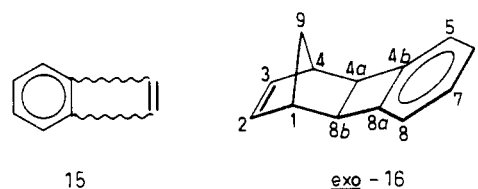


the enhanced solvolysis of **12**,²⁷ they are not apparent during the solvolysis of either **13**²⁸ or **4b**.²⁹ However, OITB facilitate the photochemical ring cleavage of the C₁-C₂ bond of **4a** to give the bisallyl radical **14**.³⁰ This observation raises the pos-



sibility that reactions involving biradical or radical intermediates are particularly sensitive to the influences of OITB. In support of this proposal we note that the Birch reduction,³¹ which involves the intermediacy of radical anions, is a sensitive chemical probe for detecting the presence of through-space interactions. Thus it is found that nonconjugated double bonds, which are normally unresponsive to this reduction,³¹ are readily reduced when they are constrained to lie in close proximity to another double bond or aromatic ring. For example norbornadiene^{32,33} and related compounds³⁴ are rapidly reduced compared with norbornene.³⁵

We have initiated a series of investigations in order to assess the efficacy of the Birch reduction as a means of detecting OITB. Our approach has been to measure the relative rates of reduction of the double bonds in the series of rigid compounds **15** in which both the length and geometry of the σ

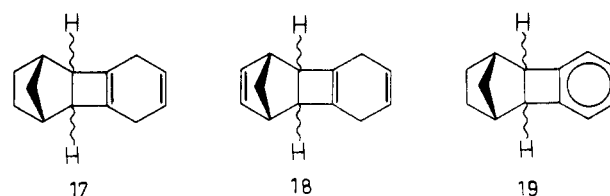


framework separating the double bond and the aromatic ring are varied systematically. In this paper we examine the Birch reductions of *exo*- and *endo*-tetrahydro-1,4-methanobiphenylenes, *exo*-**16** and *endo*-**16**, respectively, in which the orbitals of the unsaturated centers can interact through a double three-bond relay.³⁶

Results

Birch Reduction Product Studies. Unless stated otherwise all Birch reductions were carried out using a solution of lithium metal in a refluxing (ca. -33 °C) mixture of liquid ammonia, THF (cosolvent), and *tert*-butyl alcohol (proton source).

Treatment of *exo*-**16** with a large excess of lithium metal (4.5 molar equiv) for 4 h led to the formation of two products, *exo*-**17** and *exo*-**18**, in the ratio 1:1.13, respectively. Structural



identification of the products was easily confirmed on the basis of their MS, ¹H NMR, and ¹³C NMR spectral data (see Experimental Section) and from the observation that dichlorodicyano-*p*-benzoquinone (DDQ) oxidations of *exo*-**17** and *exo*-**18**, respectively, led to the quantitative formation of the aromatized compounds *exo*-**19** and *exo*-**16**.

Table I. Product Data from Birch Reductions of 16

entry	substrate	Li ^a	time, h	% yields ^b				
				16	17	18	19	18:(17 + 19)
1	<i>exo</i> -16	4.5	4.5	0	47	53	0	1.13
2	<i>exo</i> -16	4.5	1	0	27.8	72.2	0	2.6
3	<i>exo</i> -16	2	0.25	4.7	12.5	75.9	6.9	3.91
4	<i>exo</i> -16	2	0.1	21.5	4.6	62.6	11.3	3.94 ^c
5	<i>endo</i> -16	4.5	4	0	28.6	71.4	0	2.5
6	<i>endo</i> -16	2	0.25	11.2	7.8	70.2	8.1	4.4
7	<i>endo</i> -16	2	0.1	30.6	6.2	56.7	6.5	4.5 ^c

^a Molar equivalents. ^b Determined by GLC analysis of crude reduction product. ^c = $k_A:k_D$ (see text for meaning of k_A and k_D).

Table II. Relative Rate Constants for the Birch Reduction of Some Substrates

entry	substrate	competitor	k^c ^a	k^N ^b	k_D^N ^c	k_A^N ^d
1	<i>exo</i> -16	toluene	24	696	141	555
2	<i>exo</i> -18	20	0.33	1.9	1.9	
3	<i>exo</i> -19	toluene	10.4	302		302
4	<i>endo</i> -16	toluene	14.7	426	78	348
5	<i>endo</i> -18	20	0.28	1.6	1.6	
6	<i>endo</i> -19	toluene	11.2	325		325
7	20	21	5.8	5.8	5.8	
8	toluene	20	5.1	29.6		
9	toluene	21	29	29		29
10	22	toluene	0.37	10.7	10.7	

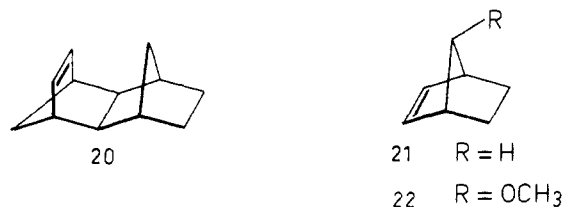
^a Overall rate constants relative to the specified competitor. ^b Adjusted rate constants relative to norbornene. ^c Rate constants for the reduction of the double bond of the substrates relative to norbornene. ^d Rate constants for the reduction of the aromatic ring of the substrates relative to norbornene.

The formation of *exo*-17 could arise from two pathways: (1) prior reduction of the double bond of *exo*-16 giving *exo*-19 and subsequent reduction of this intermediate; (2) further reduction of *exo*-18. In order to assess the relative importance of these pathways further reductions of *exo*-16 were carried out in which the amount of lithium and the reaction time were varied. The product compositions were determined by GLC and the data are summarized in Table I. Treatment of *exo*-16 with less lithium (entries 3 and 4) gave, in addition to unreacted material, a mixture of the three *exo* compounds, 17, 18, and 19. If the reaction time is increased from 0.1 h (entry 4) to 0.25 h (entry 3), the ratio *exo*-17:*exo*-19 increases from 0.4:1 to 1.8:1. Furthermore, the ratio 18:(17 + 19) is approximately the same for entries 3 and 4. The data for entries 3 and 4 lead us to conclude that *exo*-17 is being formed exclusively via the intermediacy of *exo*-19 under these conditions and that the ratio 18:(17 + 19) = 3.94:1 represents the ratio $k_A:k_D$ for the reduction of the aromatic ring (k_A) and the double bond (k_D) of *exo*-16. This ratio decreases with increasing reaction time and lithium metal concentration (entries 1 and 2) because the formation of *exo*-17 from subsequent reduction of *exo*-18 becomes important.

The reduction of *endo*-16 with lithium followed a similar pattern of behavior to that of the *exo* isomer. Using small amounts of lithium and short reaction times the ratio 18:(17 + 19) is constant at about 4.5 (Table I, entries 6 and 7) but decreases when the reaction time is increased (entry 5). Applying the same reasoning used for the *exo* isomer it is concluded that $k_A:k_D = 4.5:1$ for the Birch reduction of *endo*-16.

Competition Kinetic Studies. The competition method³⁸ was used to obtain the rate data for the reductions since relative rate constants are entirely adequate for our purposes. Krapcho and his co-workers have earlier demonstrated the viability of this technique in obtaining reliable rates of Birch reductions.^{37,39} Our results are presented in Table II. The fourth column lists the overall rate constants, k^c , for the reduction of the substrates relative to their respective competitors.⁴⁰ The k^N values are the adjusted rates of reduction relative to a

common substrate, norbornene (21). The self-consistency of these data was checked by measuring all three competitive rate constants, k^c , for the reduction of toluene, 20, and 21, taken



in pairs (entries 7–9, Table II). The predicted value of $k^c = 29.6$ for toluene vs. 21 (i.e., the product of the k^c values of entries 7 and 8) is in close agreement with the experimentally determined value of 29 (entry 9). The k^N values for the reduction of *endo*- and *exo*-16 are the sum of the individual relative rate constants for reduction at the double bond (k_D^N) and the aromatic ring (k_A^N). The latter two constants may be separately evaluated since their ratio is already known (Table I, entries 4 and 7 for *exo*- and *endo*-16, respectively).

Discussion

It is expected that any appreciable interaction between the vacant MOs of the double bond and aromatic ring in a substrate should result in noticeable changes in the rate of Birch reduction at each site relative to suitable model compounds in which such interactions are absent.

***exo*-Tetrahydro-1,4-methanobiphenylene (*exo*-16).** The double bond of this compound is reduced some 141 times faster than the double bond of norbornene (k_D^N value, Table II). Steric and strain effects cannot account for this rate enhancement since the double bonds of *exo*-16 and 21 are in structurally similar environments. This view is further supported by the observation that *exo*-18, whose strain energy is comparable to that of *exo*-16, is still ca. 70 times less reactive than *exo*-16 (k_D^N values, Table II). The enhanced reactivity of the double bond in *exo*-16 cannot be due to the $-I$ effect of the aromatic ring for the following reasons. Firstly, the k_D^N for the Birch reduction of *anti*-7-methoxynorbornene (22) is

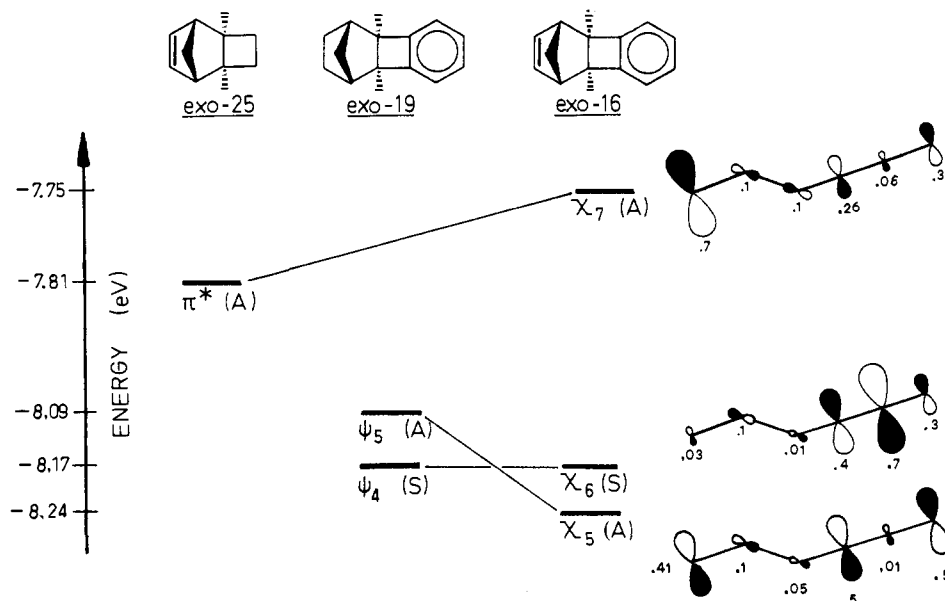
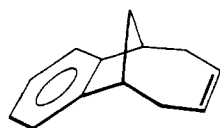


Figure 1. EHT correlation diagram showing the energies and coefficients of the lowest three vacant MOs, $\chi_5 - \chi_7$, of *exo*-16.

only 11 (Table II). Since the methoxy substituent exerts a stronger $-I$ effect than the phenyl substituent (their inductive substituent constants are 1.81 and 0.94, respectively⁴¹) we expect k_D^N for *exo*-16 to be much less than 11 if inductive effects alone were operating. Finally, PES studies on the related system **23** revealed that the ionization potential of the



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double bond was virtually unaffected by the aromatic ring,⁴² thereby demonstrating the negligible $-I$ effect of the benzene ring on a double bond three σ bonds removed.

Although the evidence so far presented has been of the eliminative kind, it appears that OITB are responsible for the enhanced k_D^N value for the Birch reduction of *exo*-16.

Surprisingly the aromatic ring in *exo*-16 is reduced only 1.8 times more rapidly than the corresponding ring in *exo*-19 (k_A^N values, Table II). However, MO calculations reveal that this unexpected result is not inconsistent with the presence of OITB in this molecule (vide infra).

endo-Tetrahydro-1,4-methanobiphenylene (endo-16). The double bond in this compound is reduced some 78 times faster than norbornene and about 2 times more slowly than the double bond in *exo*-16 (k_D^N values, Table II). Inductive and strain effects cannot account for the enhanced k_D^N of this compound for the same reasons that were advanced in the case of the *exo* isomer.

The unsaturated centers of *endo*-16 are sufficiently close (ca. 2.5 Å⁴³) to interact through space as well as through bonds. However, these interactions oppose one another ($m = 3$ is odd for this molecule, vide supra) with the result that the net interaction in *endo*-16 should be less than that in the *exo* isomer.⁴⁴ The smaller k_D^N of *endo*-16 compared with that of *exo*-16 is fully consistent with the above prediction. However, whether net through-space or through-bond interactions prevail in *endo*-16 can only be determined through MO calculations (vide infra).

As in the case of the *exo* isomer, the aromatic ring of *endo*-16 is only marginally activated, being about 1.1 times more reactive than the aromatic ring of *endo*-19 (k_A^N values, Table II).

exo- and endo-Hexahydromethanobiphenylenes (18). Birch reduction of *exo*- and *endo*-18 gave *exo*- and *endo*-17, respectively. The products were characterized through comparison of their GLC and MS data with those of authentic specimens.

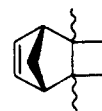
The k_D^N values of *exo*- and *endo*-18 are surprisingly small considering that appreciable orbital interactions between the double bonds have been shown to be present in the related compounds **4a**¹⁴ and **5**.¹⁵ These "anomalous" results will be discussed further in the following section.

Molecular Orbital Calculations

Some molecular orbital calculations were carried out in order to gain a deeper insight into any relationship which might exist between the presence of orbital interactions and the rates of Birch reduction of *exo*- and *endo*-16. As the rate of the Birch reduction is believed to be dependent on the ease of both formation and subsequent protonation of the radical anion of the substrate,³¹ then, within the framework of the single-electron approximation, the energy and the coefficients of the LUMO of the substrate should play a pivotal role. We therefore focus our attention on the interactions between the vacant orbitals in the appropriate molecules.

The extended Hückel (EH) method^{45,46} was used because, despite its well-known deficiencies and limitations, it has been consistently reliable in analyzing orbital interactions.^{2,3} Our choice of method is further justified by the recent work of Heilbronner and Schmelzer,⁴⁸ who demonstrated that semi-empirical SCF MO methods, such as CNDO/2 and MINDO/2, are unreliable in assessing through-space and through-bond interactions.

The EH computed eigenvectors and eigenvalues of the LUMO and the next LUMO (NLUMO) for a series of molecules are displayed in Table III.⁴⁹ The correlation diagram for the formation of the three lowest vacant MOs of *exo*-16 are shown in Figure 1. These orbitals may be thought to arise from mixing of orbitals of *exo*-25 and *exo*-19 of the same



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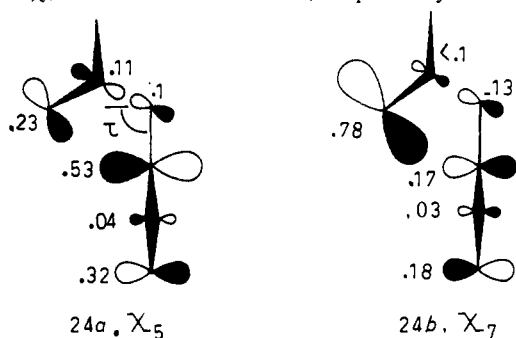
Table III. EH Eigenvectors and Eigenvalues of Frontier Orbitals

structure	sym ^b	LUMO ^a					E, eV	sym ^b	NLUMO ^a					E, eV
		C ₃	C _{4b}	C ₅	C ₆	C ₃			C _{4b}	C ₅	C ₆			
<i>exo</i> -16	A	0.41	0.49	0.01	-0.5	-8.24	S	-0.03	0.36	-0.66	0.32	-8.19		
<i>endo</i> -16 ^d	A	0.23	0.53	0.04	-0.32	-8.19	S	0.02	-0.36	0.66	-0.57	-8.17		
<i>exo</i> -19	S		0.37	-0.66	0.32	-8.15	A		0.55	0.04	-0.6	-8.09		
<i>endo</i> -19 ^d	S		0.36	-0.66	0.32	-8.17	A		0.55	0.04	-0.6	-8.09		
4a	A	0.55			0.59 ^c	-8.06	A	0.61			-0.55 ^c	-7.51		
5	A	0.53			0.6 ^c	-7.99	A	-0.62			0.54 ^c	-7.71		
<i>exo</i> -25	A	0.81 ^c				-7.77								
<i>endo</i> -25 ^d	A	0.81 ^c				-7.86								
<i>exo</i> -26	A	0.82				-7.81								
<i>endo</i> -26 ^d	A	0.82				-7.80								
21	A	0.81				-7.95								

^a Coefficients of locally transformed "π-type" p atomic orbitals. ^b A = antisymmetric, S = symmetric with respect to molecular plane of symmetry. ^c Value refers to C₇ of this molecule. ^d Results obtained with τ = 93°.

symmetry and the orbital designations given in Figure 1 reflect the origin of the MOs of *exo*-16. It is apparent from Figure 1 that extensive (symmetry allowed) mixing between the NLUMO (ψ_5) of the aromatic ring and the π^* MO of the double bond is taking place through the C_{4a}C_{4b} and C_{8a}C_{8b} σ bonds and that the resulting interaction energy⁵¹ is quite large (0.2 eV). Note that χ_5 contains a sizable contribution from the π^* MO of the double bond and it certainly *cannot* be considered to be a slightly perturbed benzene MO. A calculation on *exo*-16 in which all overlap integral matrix elements between the carbon basis orbitals and those of the aromatic ring were neglected left the coefficients and energies of χ_5 - χ_7 unchanged, thereby demonstrating the through-bond origin of these interactions.

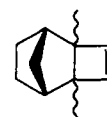
The energies of the unoccupied MOs of *endo*-16 were found to depend on the value of the angle, τ , between the planes defined by the aromatic ring and the atoms C₂C₃C_{4a}C_{8b} (see **24**). The interaction energy arising from mixing of the basis MOs π^* and ψ_5 (to give χ_5 and χ_7) increases with decreasing values of τ or, equivalently, with decreasing separation between the double bond and the aromatic ring. This behavior is symptomatic of net through-space dominated interactions and its presence is confirmed through inspection of the topologies of χ_5 and χ_7 shown in **24a** and **24b**, respectively. Thus χ_5 is



generated from the bonding admixture of π^* into ψ_5 , whereas the higher energy MO χ_7 is formed from the corresponding antibonding admixture of ψ_5 into π^* . The geometry of *endo*-16 probably corresponds to $\tau = 93^\circ$,⁵² in which case the net interaction energy is 0.16 eV. The presence of competing OITB in *endo*-16 was revealed by a calculation in which through-space interactions were neglected in the manner described above for *exo*-16. The resulting interaction energy of 0.34 eV (χ_7 is now the LUMO) is a measure of the OITB contribution. The (opposing) OITS contribution is therefore 0.5 eV.

The results for **4a** and **5** were similar to those for *exo*- and *endo*-16, respectively (Table III), i.e., an OITB interaction energy of 0.51 eV (with respect to the π^* basis MOs of *exo*-25 and *exo*-26) in **4a** and a net OITS interaction energy of 0.22

eV (with respect to the π^* MOs of *endo*-25 and *endo*-26) in **5**.



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How are orbital interactions expected to affect the rate of Birch reduction of a substrate? Application of the commonly accepted^{31,37,39} mechanism of the Birch reduction to the reduction of a substrate **27** containing a double bond, D, whose orbitals interact with those of an aromatic ring, A, is shown in Scheme 1. Addition of an electron to **27** generates a single radical anion **28** in which, by virtue of the presence of orbital interactions, the unpaired electron density is distributed over both D and A. Irreversible protonation⁵³ of **28** may occur either at D or A to give the respective radicals **29** or **32**. These species react further to give eventually **31** (reduction of D) and **34** (reduction of A). Application of the steady-state approximation to this scheme together with the assumption that $k_{-1} \gg k_d, k_a$ leads to the expressions⁵⁵

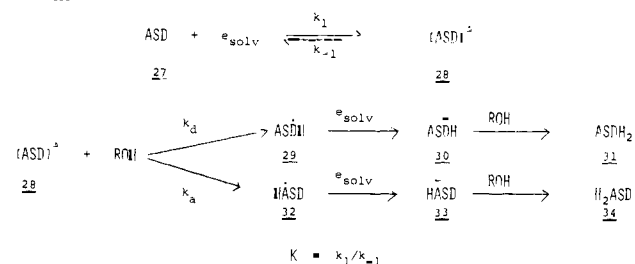
$$k_D = Kk_d \quad (1)$$

$$k_A = Kk_a \quad (2)$$

where k_D and k_A are the observed rate constants for the reduction of **27** at D and A, respectively, K is the equilibrium constant for the formation of radical anion **28**, and k_d and k_a are the rate constants for the protonation of **28** at D and A, respectively. Thus the reduction involves a rapid, reversible formation of a radical anion followed by a rate-determining protonation of this species.

Orbital interactions which cause the LUMO energy to be lowered are expected to *increase* the magnitude of K since the latter depends, among other factors,⁵⁶ on the electron affinity of the substrate. However, the same interactions are expected to result in a *decrease* in the values of k_d and k_a , as the following PMO argument demonstrates. Consider the early

Scheme I



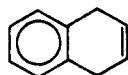
stages of protonation of a radical anion by an alcohol.⁵⁷ The dominant stabilizing interaction is between the singly occupied MO (SOMO) of the radical anion and the OH σ^* MO of the alcohol because these orbitals are separated by the smallest energy gap.⁵⁹ The stabilization energy, δE , resulting from this interaction is given to the second order by^{60,61}

$$\delta E \propto \frac{(C_i^S)^2}{E_S - E_{\sigma^*}} \quad (3)$$

where C_i^S is the SOMO p orbital coefficient of the i th carbon atom at which protonation is occurring and E_S is the energy of the SOMO of the radical anion. The SOMO energy and coefficients may be approximated by those of the LUMO of the neutral precursor. The data in Table III reveal that, with respect to **21**, OITB in *exo*-**16** lead to a decrease in the LUMO coefficients of the double-bond carbon atoms and in the LUMO energy, both of which reduce δE .⁶² Therefore k_d for *exo*-**16** should be less than that for **21**. The diminution in the LUMO coefficients at C₂ and C₃ of *exo*-**16** is a necessary consequence of the fact that the LUMO of this molecule (which is normalized) is delocalized over more atoms compared with that in **21**. The above conclusions also hold true for the other molecules studied herein.

Therefore, because orbital interactions have opposite effects on K and k_d (k_a), the overall rate of reduction will not be affected to the degree that might have been expected from the presence of such interactions. The relatively small enhanced rates of reduction of *exo*- and *endo*-**16** are therefore understandable. Because k_D and k_A for *exo*- and *endo*-**16** are enhanced, we conclude that orbital interactions are mainly manifested through their effect on K , or equivalently through their influence on the LUMO energies of the substrates. In other words, the rate of reduction of a substrate is largely determined by its LUMO energy. Thus the much lower LUMO energies of *exo*- and *endo*-**16** compared with **21** result in significantly enhanced k_D^N values for the reduction of the former pair of compounds. However, the closeness of the LUMO energies of *exo*- and *endo*-**16** to those of *exo*- and *endo*-**19**, respectively, leads to only marginally enhanced rates of aromatic ring reduction of the former two compounds. Despite the presence of appreciable orbital interactions in *exo*- and *endo*-**18** the LUMO energies of these molecules (which have been approximated by those of **4a** and **5**, respectively) are only slightly less than that of **21** but greater than those of *exo*- and *endo*-**16**. The smaller k_D^N values of the reduction of the former two substrates are thereby explained.

The dependence of the rate of Birch reduction on the substrate LUMO energy is supported by the observation of a reasonably linear relationship between $\ln k^N$ and the LUMO energy, E_L , for a series of substrates (Figure 2). The E_L values of *exo*- and *endo*-**18** have been approximated by those of **4a** and **5**, respectively. The datum point for 1,4-dihydronaphthalene (**35**) ($\ln k^N = 4.78$, $E_L = -8.14$ eV) was obtained from



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a different study.⁵⁵ Linear regression analysis of these data leads to the relationship

$$\ln k^N = -26.82E_L - 213.8 \quad (4)$$

with a correlation coefficient of 0.955. A linear relationship of this type is expected to hold provided that $\ln K \propto E_L$. From this expression we predict that k_D^N for norbornadiene ($E_L = -8.46$ eV) should be about 5×10^5 . The experimentally determined value⁶³ of 10^5 is in reasonable accord with this prediction.

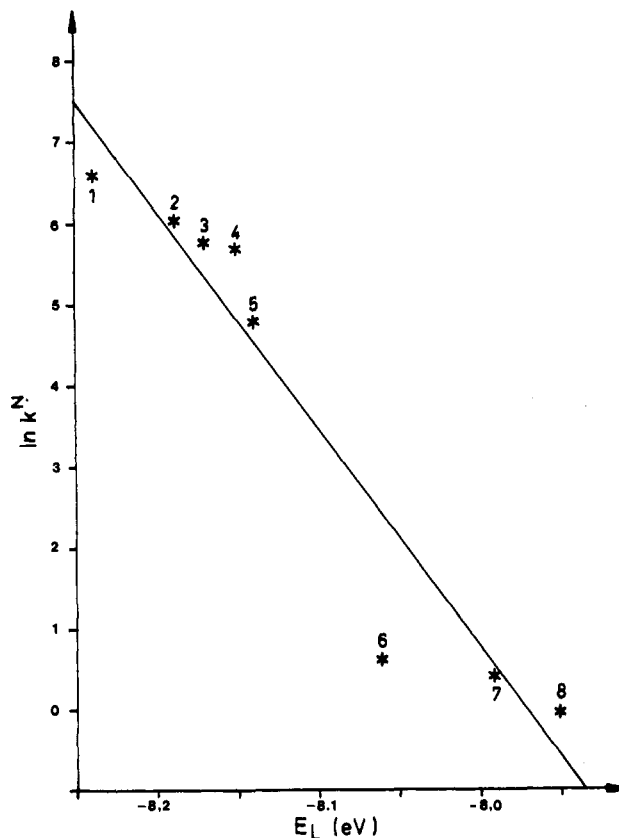


Figure 2. Plot of $\ln k^N$ vs. E_L for the Birch reduction of a series of substrates: 1 = *exo*-**16**; 2 = *endo*-**16**; 3 = *endo*-**19**; 4 = *exo*-**19**; 5 = **35**; 6 = *exo*-**18**; 7 = *endo*-**18**; 8 = **21**.

In conclusion it appears that orbital interactions do affect the rate of Birch reduction in a predictable manner and that this reaction offers considerable scope for exploring the nature of such interactions.⁶⁴ In the accompanying paper we apply the Birch reduction to the investigation of OITB extending over four or more σ bonds.

Experimental Section

All melting points are corrected and were recorded on an Electrothermal melting point apparatus in capillary tubes. Boiling points are uncorrected.

¹H NMR spectra (60 MHz) were recorded on a Varian T60 instrument and the 100-MHz ¹H NMR spectra were recorded on a JEOL PS100 spectrometer; deuteriochloroform was used as solvent with tetramethylsilane (Me₄Si) employed as the internal standard. Chemical shifts are reported in parts per million (δ) relative to Me₄Si. ¹³C NMR spectra were obtained on the JEOL PS 100 instrument operating at 25.15 MHz in the pulse Fourier mode. Deuteriochloroform was employed as the solvent and internal lock with chemical shifts being measured relative to Me₄Si.

GLC analyses were performed on a Bendix 1200 instrument using a flame ionization detector. Preparative separations were carried out using a Pye 105 machine.

The following columns were employed in the analytical, preparative, and GC/MS phases of the work: (A) 2 m \times 3 mm stainless steel containing 3% OV-1 on Gas-Chrom Q 60/80; (B) 8 m \times 3 mm aluminum containing 7.5% Carbowax 20M on Chromosorb W (AW) 60/80; (C) 2 m \times 3 mm stainless steel containing 10% SE-30 on Chromosorb W (AW) 60/80; (D) 4.2 m \times 12 mm glass containing 10% SE-30 on Chromosorb W (AW) 60/80; (E) 4 m \times 3 mm stainless steel containing 7.5% OV-17 on Chromosorb W (AW) 60/803 joined to column B with 3-mm Swagelock union filled with 7.5% OV-17 on Chromosorb W (AW) 60/80.

The flow rates were 60 mL min⁻¹ unless stated otherwise.

Mass spectra were measured on an AEI MS902/Pye 105 GC/MS system, operating at 22 or 75 eV.

exo-1,4,4a,8b-Tetrahydro-1,4-methanobiphenylene (exo-16). The overall synthetic strategy of Simmons⁶⁶ was followed except that benzyne was generated using the method of Watson and Warrener.⁶⁷ Norbornadiene (138 g, 1.5 mol) and dry dioxane (220 mL) were heated to a gentle reflux. Solutions of anthranilic acid (61.5 g, 0.45 mol) in dioxane (180 mL) and freshly distilled isopentyl nitrite (55 g, 0.45 mol) in dioxane (180 mL) were added simultaneously, dropwise, to the stirred refluxing solution over a period of 1 h. The solution was refluxed for an additional 1 h followed by cooling and the adjustment of its pH to 8 with 2 M NaOH. The resulting solution was extracted with petroleum spirit (bp 60–80 °C, 3 × 200 mL). Evaporation of the solvent and distillation of the residue (70–80 °C, 0.5 mmHg) gave a clear oil which contained *exo-16* and the benzyne-norbornadiene "homo" adduct⁶⁸ in the ratio of 2:1, respectively (GLC, column C, 125 °C). The crude yield of adducts was 33 g. Resolution of the mixture into its components was achieved through silver complexation of *exo-16*. The mixture was added to a magnetically stirred saturated aqueous solution of AgNO₃ (20 mL). The silver complex was collected by filtration. (Extraction of the filtrate with ether and evaporation of the solvent gave essentially pure "homo" adduct.) The complex was dissolved in water (400 mL) at 55 °C followed by the addition of saturated NaCl (100 mL). The mixture was filtered. The silver complex was triturated with petroleum spirit (bp 60–80 °C, 3 × 200 mL). The filtrate was also extracted with the same solvent (2 × 50 mL). The combined extracts were washed with water (50 mL), dried (Na₂SO₄), and distilled (49 °C, 0.3 mmHg) to give *exo-16* (15.5 g, 21%) which had identical spectral properties with those reported.^{66,69}

endo-1,4,4a,8b-Tetrahydro-1,4-methanobiphenylene (endo-16) was prepared by the method of Nenitzescu et al.⁷⁰

exo- and endo-1,2,3,4,4a,8b-Hexahydro-1,4-methanobiphenylenes (exo- and endo-19) were prepared by the catalytic hydrogenation of the respective isomers of 16 as described by Simmons.⁶⁶

anti-7-Methoxynorbornene (22) was prepared by the method of Meinwald et al.⁷¹ as modified by Brown,⁷² bp 90–91 °C (150 mmHg) (lit.⁷¹ 91–92 °C, 160 mmHg).

exo,endo-1,4,4a,5,6,7,8,8a-Octahydro-1,4:5,8-dimethanonaphthalene (20) was prepared by the method of Stille and Witerell.⁷³

Birch Reductions, Reagents and Equipment. Lithium metal (BDH) was pressed through a 1-mm die and stored under liquid paraffin. A series of lengths was measured and weighed, thus calibrating the weight per length. Immediately prior to use a small section was cut off and washed with pentane. A measured length, of known weight, was sliced off with a new stainless steel spatula blade and added to the reaction mixture under a positive nitrogen pressure. Tetrahydrofuran (THF, Ajax Chemicals, Univar Grade) was refluxed over lithium aluminum hydride, immediately prior to use, in a modified Dean-Stark apparatus.⁵⁵ The anhydrous THF was collected under nitrogen in a flask with a drying tube attached to exclude moisture. *tert*-Butyl alcohol (TBA) was purified by distillation from metallic sodium. Norbornene (Aldrich) was recrystallized from methanol and then the wet crystals were pressed between filter paper to remove excess solvent. The material was then dissolved in pentane and passed down an alumina column (1/2 × 3 in.), with the solvent being subsequently removed by warming at atmospheric pressure, under a Vigreux column. The GLC analysis of the product (column C, 25 °C, flow 19 mL min⁻¹) showed the contaminating norbornane content to be less than 0.05%. Pentane (Ajax, Univar) and toluene (Mallinckrodt, Spectrar) were supplied sufficiently pure (GLC) to be used without further purification.

Commercial anhydrous ammonia (Commonwealth Ammonia) was purified prior to use in the following way: distillation from the tank into a flask containing sodium metal (ca. 4 g) and anhydrous ferric chloride (100 mg) and subsequent redistillation into the reaction flask under a positive pressure of dry nitrogen.

All Birch reductions were carried out in a graduated 250-mL Erlenmeyer flask fitted with a ground glass joint and containing a glass-encapsulated magnetic stirring bar. The flask was connected to a three-necked adaptor for the nitrogen and reactant inlets and the acetone-dry ice charged condenser. The outlet of the condenser was fitted with a soda lime guard tube. The apparatus was continually flushed with dry nitrogen. Prior to carrying out a reduction, all glassware was cleansed by washing with copious quantities of ca. 1% aqueous triethylamine and finally washing with freshly deionized water. The glassware was dried overnight in an oven at 120 °C. The

assembled apparatus was flame dried and Parafilm was employed to seal all joints.

Individual Birch Reductions. The general procedure is as follows. To a magnetically stirred solution of the substrate (ca. 5 mmol) in refluxing liquid ammonia (ca. 100 mL) and THF (ca. 20 mL) was added the appropriate amount of lithium followed by the addition of TBA (1.4 g, 19 mmol). The mixture was stirred at reflux for the required period after which the reaction flask was cooled to -78 °C. Pentane (10 mL) was added followed by dropwise addition of saturated aqueous ammonium chloride (ca. 500 mL) over 1 h. The mixture was warmed to -10 °C and the organic layer was collected. The aqueous residue was extracted with pentane (2 × 50 mL). The combined extracts were washed with water (2 × 50 mL), dried (Na₂SO₄), and evaporated.

A. Reduction of exo-16. This compound was reduced in four runs (30 mmol of substrate, 600 mL of NH₃, 120 mL of THF, and 180 mmol of TBA) and the reaction times and product data are given in Table I. Two products were formed using 4.5 molar equiv of Li which were separated by GLC (column D, 125 °C). The major isomer was identified as **exo-1,2,3,4,4a,5,8,8b-octahydro-1,4-methanobiphenylene (exo-17)**: ¹H NMR (CDCl₃) δ 0.75–1.70 (6 H, m, H₂, H₃, H₉), 2.0 (2 H, t, *J* = 1 Hz, H₁, H₄), 2.55 (6 H, s, H_{4a}, H₅, H₈, H_{8b}), 5.78 (2 H, s, H₆, H₇); ¹³C NMR (CDCl₃, ¹H decoupled) δ 19.3 (2 C, C₅, C₈), 23.03 (2 C, C₂, C₃), 26.13 (1 C, C₉), 28.7 (2 C, C_{4a}, C_{8b}), 46.09 (2 C, C₁, C₄), 20.57 (2 C, C₆, C₇), 134.93 (2 C, C_{4b}, C_{8a}); mass spectrum *m/e* (rel intensity) 172 (M⁺, 9.8), 143 (12.2), 132 (12.2), 131 (100), 130 (19.5), 129 (59.1), 125 (12.1), 118 (14.2), 117 (19.4), 116 (15.8), 104 (12), 92 (17.4), 91 (27), 81 (25.2), 80 (13.5), 79 (14.2).

The minor product was identified as **exo-1,4,4a,5,8,8b-hexahydro-1,4-methanobiphenylene (exo-18)**: ¹H NMR (CDCl₃) δ 1.36 (2 H, t, *J* = 1 Hz, H₉), 2.46 (2 H, s, H₁, H₄), 2.52 (2 H, s, H_{4a}, H_{8b}), 5.75 (2 H, s, H₆, H₇), 6.09 (2 H, t, *J* = 1 Hz, H₂, H₃); mass spectrum *m/e* (rel intensity) 171 (4.4), 170 (M⁺, 20.8), 169 (13.7), 155 (42.9), 153 (11.0), 142 (15.5), 141 (28.6), 129 (58.8), 128 (25.0), 117 (11.8), 116 ((M - butadiene)⁺, 100.0), 115 (17.5), 105 (32.7), 104 (29.6), 103 (26.4), 102 (11.0), 92 (24.3), 91 (30.8), 79 (57.2), 78 (49.6), 77 (14.4), 66 (18.1).

The mixture resulting from the reduction of *exo-16* using 2 molar equiv of Li (entry 4, Table I) was subjected to preparative GLC (column B, 12 m × 12 mm, 125 °C) and two fractions were isolated. ¹H NMR analysis revealed that one fraction consisted of *exo-16* and *exo-19* and the other fraction consisted of *exo-17* and *exo-18*. Preparative GLC (column D, 125 °C) on the former fraction led to the isolation of *exo-19* which was identical in every respect with authentic material.

Product yield data of Table I were obtained by GLC analysis (column E, 70–120 °C at 4 °C/min; held at 120 °C for 10 min, then increased to 170 °C at 4 °C/min and held at this temperature).

B. Reduction of endo-16. This compound was reduced in three runs (20 mmol of substrate, 400 mL of NH₃, 80 mL of THF, and 180 mmol of TBA) and the reaction times and product data are given in Table I. Two isomeric products were formed using 4.5 molar equiv of Li which were separated by GLC (column D, 125 °C). The major isomer was identified as **endo-1,4,4a,5,8,8b-hexahydro-1,4-methanobiphenylene (endo-18)**: ¹H NMR (CDCl₃) δ 1.55 (1 H, d, *J* = 8 Hz, H_{9syn}), 1.91 (1 H, d, *J* = 8 Hz, H_{9anti}), 2.48 (4 H, s, H₅, H₈), 2.62 (2 H, m, H₁, H₄), 3.05 (2 H, d, *J* = 3 Hz, H_{4a}, H_{8b}), 5.72 (2 H, s, H₆, H₇), 5.82 (2 H, t, *J* = 1 Hz, H₂, H₃); mass spectrum *m/e* (rel intensity) 170 (M⁺, 35.2), 169 (19.2), 155 (60.1), 154 (12.2), 153 (11.9), 142 (20.6), 141 (37.3), 129 (69.7), 128 (28.4), 117 (11.6), 116 (M - butadiene)⁺, 100.0), 115 (18.0), 105 (19.1), 104 (24.3), 103 (18.9), 92 (36.8), 79 (39.7), 78 (28.7).

The minor product was identified as **endo-1,2,3,4,4a,5,8,8b-octahydro-1,4-methanobiphenylene (endo-17)**: ¹H NMR (CDCl₃) δ 1.30 (4 H, m, H₂, H₃), 1.58 (2 H, s, H₉), 2.18 (2 H, br s, H₁, H₄), 2.62 (4 H, s, H₅, H₈), 2.93 (2 H, m, H_{4a}, H_{8b}), 5.79 (2 H, s, H₆, H₇); mass spectrum *m/e* (rel intensity) 172 (M⁺, 15.8), 143 (10.4), 132 (11.0), 131 (100.0), 130 (18.4), 129 (36.3), 118 (12.3), 117 (14.1), 92 (10.8), 91 (16.3), 81 (15.4). The other peaks were less than 10%. Oxidation with DDQ gave *endo-19*, which was identified by ¹H NMR and GLC/mass spectral analysis.

Reduction of *endo-16* (20 mmol) using 2 molar equiv of Li and the same quantities of other reagents as above led to the formation of the four endo compounds 16–19. Isolation of *endo-19* and the determination of product yields (Table I) were carried out using the same

Table IV. Details of the Blank Birch Runs

components	initial molar composition		GLC analytical details	molar composition of pentane extract	
	A:B	C:D		A:B	C:D
A: 21	2.07		column C ^a	2.19	
B: norbornane					
C: toluene		14.5	column A ^b		14.9
D: 2,5-dihydrotoluene					
A: 22	4.48		column A ^c	4.55	
B: 7-methoxynorbornane					
C: toluene		14.5	column A ^b		14.9
D: 2,5-dihydrotoluene					
A: 21	2.07		column C ^a	2.19	
B: norbornane					
C: 20		1.50	column A ^d		1.50
D: perhydrodimethanonaphthalene					
A: toluene	14.5		column A ^b	14.9	
B: 2,5-dihydrotoluene					
C: 20		1.50	column A ^d		1.57
D: perhydrodimethanonaphthalene					

^a 25 °C isothermal, 10 mL min⁻¹. ^b 30 °C isothermal, 60 mL min⁻¹. ^c 60 °C isothermal, 60 mL min⁻¹. ^d 190 °C isothermal, 60 mL min⁻¹.

techniques and columns as described above for *exo*-**16**.

C. Reduction of *exo*- and *endo*-19**.** Separate treatment of these compounds (30 mmol) with a large excess of Li (10 mmol) (NH₃ (600 mL), THF (100 mL), and TBA (200 mmol)) led to the formation of a single product in each case: *exo*-**17** from *exo*-**19**, and *endo*-**17** from *endo*-**19**. These products were identical in all respects with those isolated from the exhaustive reduction of the respective *exo*- and *endo*-**16** compounds.

D. Reduction of *exo*- and *endo*-18**.** Each compound (5 mmol) was treated with 10 molar equiv of Li (NH₃ (100 mL), THF (20 mL), and TBA (180 mL)) over 4 h. GLC analysis (column C, 125 °C) of the residue after workup revealed that only 10% reduction had occurred in each case to give *exo*-**17** (from *exo*-**18**) and *endo*-**17** (from *endo*-**18**). Identification of these products was achieved through the comparison of their GLC (10% Apiezon L on Chromosorb W (AW), 150 °C; 10% dinonyl phthalate on Chromosorb W (AW), 120 °C) and GLC/MS data with those of the authentic materials.

E. Reduction of **20 and **22**.** These compounds were only about 10% reduced after 4 h (conditions identical with those described in D above). Comparison of GLC (column A, 90 °C for reduction of **20**; 60 °C for reduction of **22**) and GLC/MS data with those of authentic samples revealed that *exo*,*endo*-perhydro-1,4:5,8-dimethanonaphthalene and 7-methoxynorbornane were the exclusive products of the Birch reduction of **20** and **22**, respectively.

DDQ Oxidations. The general method involved treating the substrate (ca. 1 mmol) in CHCl₃ (10 mL) with DDQ (ca. 1.2 mmol). The mixture was refluxed for 15 min, then cooled and filtered. The solvent was removed and the residue was analyzed (GLC, GLC/MS, ¹H NMR). In this way the following conversions were carried out: *exo*-**18** → *exo*-**16** (95%); *endo*-**18** → *endo*-**16** (97%); *exo*-**17** → *exo*-**19** (94%); *endo*-**17** → *endo*-**19** (99%).

Competition Kinetics. The same equipment was used for the competition kinetics as for the individual reductions (vide supra). The general procedure for carrying out the competition work is as follows. A solution of approximately equimolar amounts of the competing substrates (0.5 mmol each) in THF (5 mL) was added to the liquid ammonia (75 mL). The substrates completely dissolved in the ammonia. Lithium metal (1 mmol) was added followed immediately by the addition of TBA (1.4 g, 19 mmol) in THF (1 mL). The solution was magnetically stirred under reflux (ca. -33 °C) until the blue color had faded. The solution was cooled to -78 °C and pentane (10 mL) was added followed by dropwise addition of saturated aqueous ammonium chloride (150 mL) over 1 h. After the addition was completed the resulting solution was warmed to ca. -10 °C and transferred to a separating funnel, and the pentane layer was isolated (after rapid shaking of the solution). The pentane extract was washed once with ice-cold water (20 mL), dried, and then stored in a septum-sealed bottle. The extract was then analyzed by GLC. Product compositions were obtained from the ratios of the peak areas. The accuracy of this method was checked by analyzing mixtures of *exo*-**16** and *exo*-**19** of known composition by GLC. It was found that the ratio of the peak

areas accurately reflected the composition of the mixture over a wide range of compositions (correlation coefficient 0.997). That the product-substrate composition of the pentane extract was identical with that in the liquid ammonia immediately prior to workup was verified by performing a number of blank reductions. Thus mixtures of substrates and their reduced products of known composition were subjected to the conditions of the Birch reduction as described above except with the omission of lithium. The liquid ammonia solutions were worked up in the usual manner and the pentane extracts were analyzed by GLC. The data are given in Table IV. It is seen that differential loss of materials through their partitioning between aqueous ammonia and pentane is negligible.

The ratio of the rate constants, *k* and *k'*, for the reduction of two substrates may be obtained from the expression³⁸

$$\frac{k}{k'} = \frac{\ln(s/s_0)}{\ln(s'/s'_0)}$$

where the subscript zero refers to the concentrations (*s* or *s'*) at some initial time, *t*₀. Specific details concerning individual competitive studies may be obtained from the authors upon request. Briefly, the product mixtures resulting from the competitive reductions of the following substrates were analyzed as indicated: *exo*-**16** (column E, 70-120 °C at 4 °C/min; held at 120 °C for 10 min, then increased to 170 °C at 4 °C/min and held at this temperature); *endo*-**16** (column E, same conditions as for *exo*-**16**); *exo*-**18** (column B, 150 °C); *endo*-**18** (column B, 150 °C); *exo*-**19** (column B, 150 °C); *endo*-**19** (column B, 150 °C); **20** (column A, 90 °C); **21** (column D, 25 °C isothermal, flow rate 10 mL min⁻¹); **22** (column A, 60 °C); toluene (column A, 30 °C).

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